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25X1

FINAL REPORT

on the

THERMOELECTRIC GENERATOR PROJECT

Covering the Period

August 4, 1958 through June 1, 1959

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I. ABSTRACT

The design and construction of a twenty-couple thermoelectric generator, using zinc antimonide and n-type lead telluride as the active materials, is presented. With a hot-junction temperature of 350° and a cold-junction temperature near the boiling point of water, the device has produced nearly two watts of available electric power. Details of measurement techniques for evaluation of materials are described. Suggestions for design and construction of thermoelectric generator containing 240-couples and producing approximately 25 electrical watts of power are presented.

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II. PURPOSE OF THE STUDY

The purpose of this project is to extend the technology of small, portable thermoelectric generators to include a twenty-couple zinc antimonide-lead telluride generator which can serve as a prototype for the construction of larger assemblies.

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III. INTRODUCTION

The present development program was an outgrowth of another, whose objective was to prove the feasibility of constructing small, portable thermoelectric generators. In the previous program, a twenty-couple thermoelectric generator had been constructed to serve as a prototype for the fabrication of a generator containing 240 thermoelectric couples. The present study was intended to improve the performance of the resultant device, by modifications in materials, design, and construction procedure.

The two twenty-couple generators may be compared by referring to Table I. In order to realize the improved performance potentially available as a result of the change in the materials of construction, it was necessary to modify the design of the container, to reduce the electrical resistance of the leads, and to control the properties of the materials employed within narrow limits. The balance of this report will deal with these several aspects of the construction of the device, and with the performance of the completed twenty-couple generator.

TABLE I

PROPERTIES OF TWENTY COUPLE GENERATORS

	Previous Model	Present Model (as designed)
Number of couples	20	20
p-type material	Zinc antimonide (ZnSb)	Zinc antimonide (ZnSb)
n-type material	Advance (43% Ni, 57% Cu)	Lead Telluride (PbTe)
Hot-junction Temperature (T_h)	350° C	350° C
Cold-junction temperature (T_c)	100° C (max)	100° C (max)
Approximate figure of merit	1.0×10^{-3} °C^{-1}	1.5×10^{-3} °C^{-1}
Open-circuit voltage under designed temperature conditions	1.1 volts (measured)	2.2 - 2.4 volts (designed)
Short-circuit current under designed operating conditions	3.2 amperes (adjusted)	3.0 amperes (designed)
Maximum power output under designed operating conditions	0.9 watts (adjusted)	1.7 - 1.8 watts (designed)
Efficiency under operating conditions	1.7% (measured)	6% (theoretical)

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IV. DESIGN OF TWENTY-COUPLE GENERATOR

Modifications in design embodied in the present device stemmed from two sources. First, because of the change from Advance alloy to lead telluride for the n-type material, several changes in technique were required. Second, it was desired to eliminate causes of diminished output and reduced efficiency which were observed in the previous model. This section will deal with modifications introduced for both reasons.

A. Method of Connection Figure 1 is a photograph which illustrates the method of connection between individual arms and couples in the generator itself. Short lengths of copper wire are spot-welded to the adjacent hot or cold ends of the arms to be joined. A jig was prepared which held the pieces in the desired position for joining, assuring the one-millimeter spacing between contact pieces. The jig also permitted accurate placement of the nickel-plated copper connecting wire, so that it introduced a minimum of extraneous electrical resistance. Because the contact pieces were quite uniform in size, it thereby became possible to connect "strings" of bonded pieces of zinc antimonide and lead telluride with relative ease.

Figure 2 shows the complete generator surrounded by its protective "fence". The photograph shows the twisting of the contact pieces at the ends of individual rows of couples. This slight distortion of the normal configuration was introduced to facilitate the interconnection of the rows without the use of excessive lengths of copper wire.

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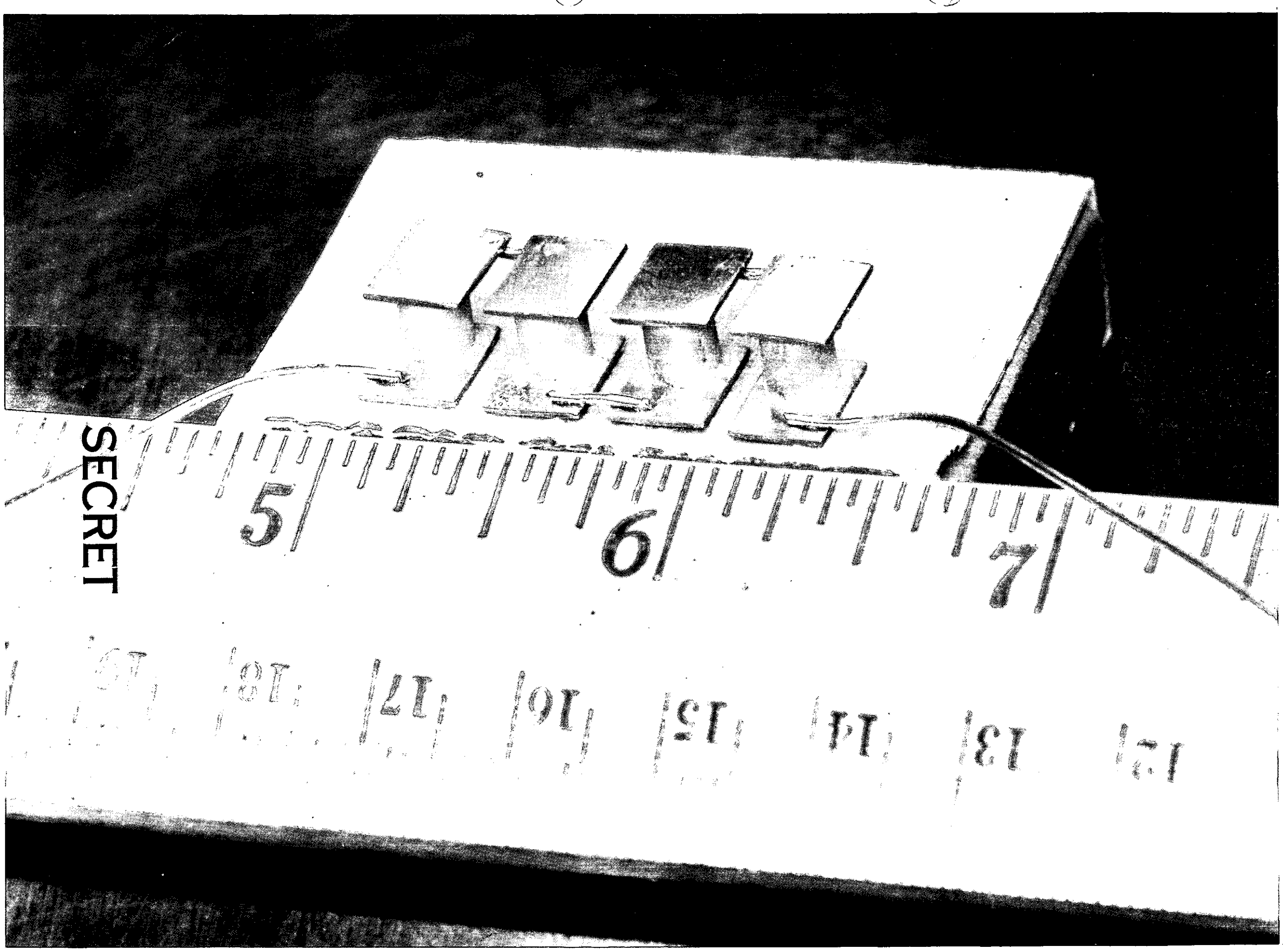

METHOD OF CONNECTION USED IN GENERATOR ASSEMBLY

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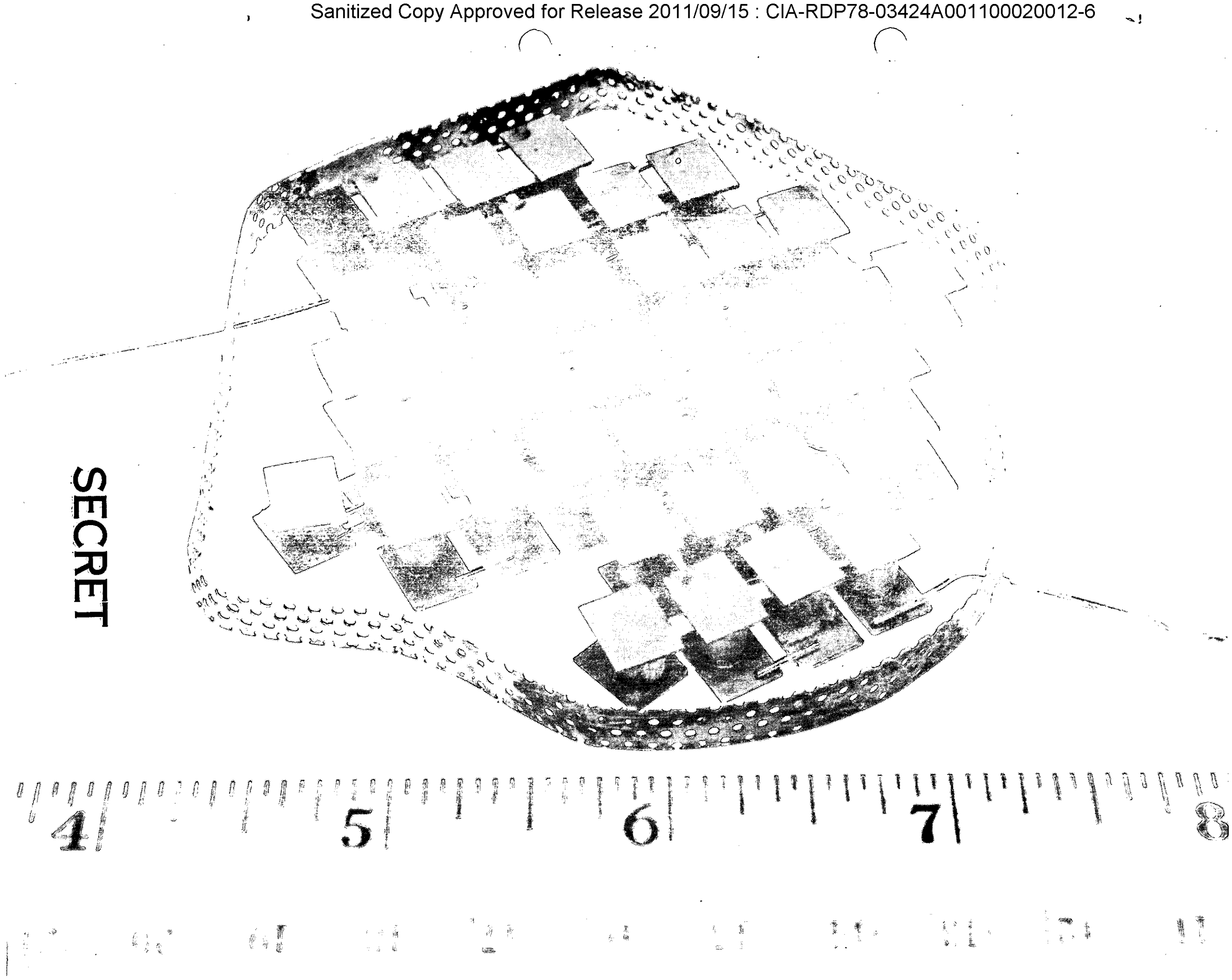

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LAYOUT OF THERMOELECTRIC GENERATOR SHOWING METHOD OF CONNECTION AND PROTECTIVE "FENCE"

FIGURE 2

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B. Assembly and Insulation It was not desired to increase the area inside the container which was occupied by the thermoelectric generator. Since the previous model contained 20 pieces of semiconducting material, and the present device was to contain 40, efficient utilization of the flat area inside the container was of paramount importance. A configuration roughly approximating a circle was adopted, as may be seen in Figure 2. There are additional advantages resulting from the circular array. The heat reaching the lower pan of the container is distributed more uniformly throughout the generator than was possible with the previous, rectangular shape. In addition, the approximation of a circle renders more uniform the forces exerted on the individual arms as a result of the evacuation of the space between the pans. These two factors combine to diminish the chances of failure of the device through overheating of an individual arm or through excessive local compressive forces.

The problems of electrical insulation were greatly simplified by a radical change in approach. Previously, thin mica sheets had served to prevent contact between the generator and the hot side of the container. On the cold side, a combination of organic resins had served the same purpose. There resulted several complications in the assembly procedure, as well as appreciable thermal resistances between the generator and the container. It was desired to retain the good electrical insulating features while diminishing the thermal insulation.

To accomplish this objective, anodized aluminum sheets were employed on both the hot and the cold sides of the generator as electrical insulation, as is shown in Figure 3, The thin (less than 0.0001 inch) layers of aluminum oxide on both sides of the 0.016-inch aluminim sheets afforded the desired electrical insulation and stability at high temperatures, while interposing a negligible thermal resistance. Any thermal impedance appearing at the interface between the contact pieces and the anodized aluminum was diminished by application of an extremely thin layer of silicone grease (Dow-Corning 11 Compound, stable at high temperatures) to the surfaces of the contact pieces just prior to the assembly.

C. Supporting Ring and Container In order to avert any crushing of the pieces of semiconductor at the periphery of the generator, a supporting ring of perforated nickel sheet (0.010 inch thick) was placed around it. The resulting configuration and its placement between the containers can be seen in Figure 4. The contours of the supporting ring were intended to keep it as close to the generator as was possible without actually coming into contact with it. When the other half of the container was placed over the assembly, it made contact with both 'pans', tending to keep them apart.

The advantages of providing protection against crushing are mitigated by the introduction of a thermal 'leak' from the hot to the cold side of the generator. In the previous model, hollow cylinders of stainless steel were used for support. It was found, however, that

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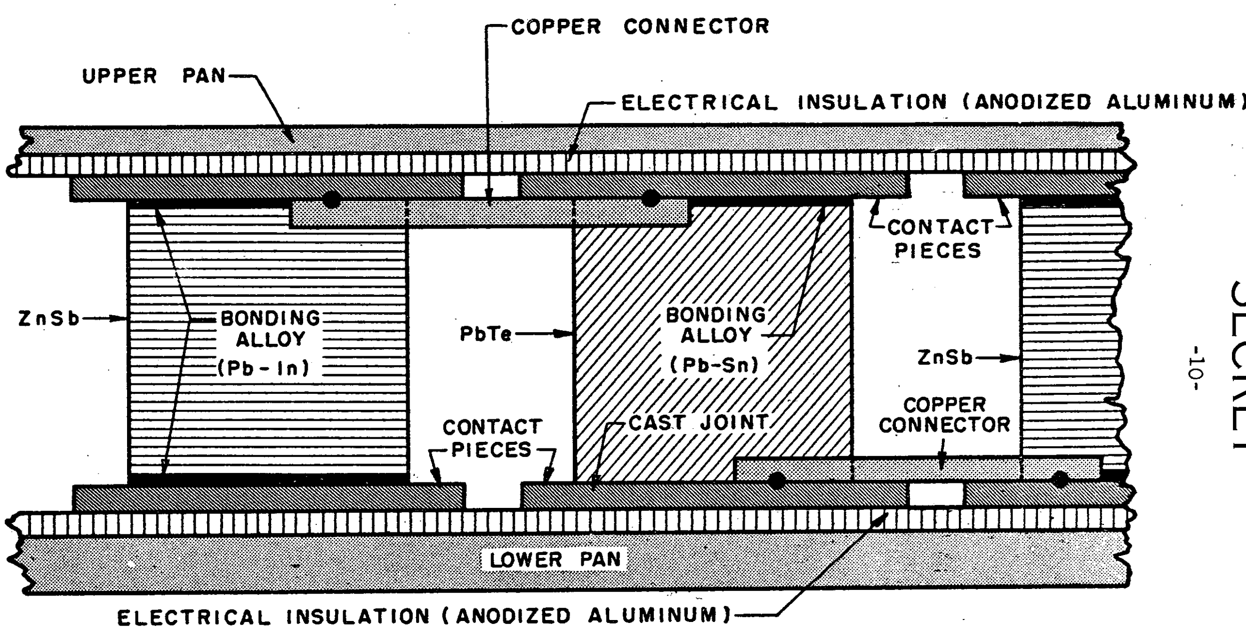

SECTION TROUGH THERMOELECTRIC GENERATOR

FIGURE 3

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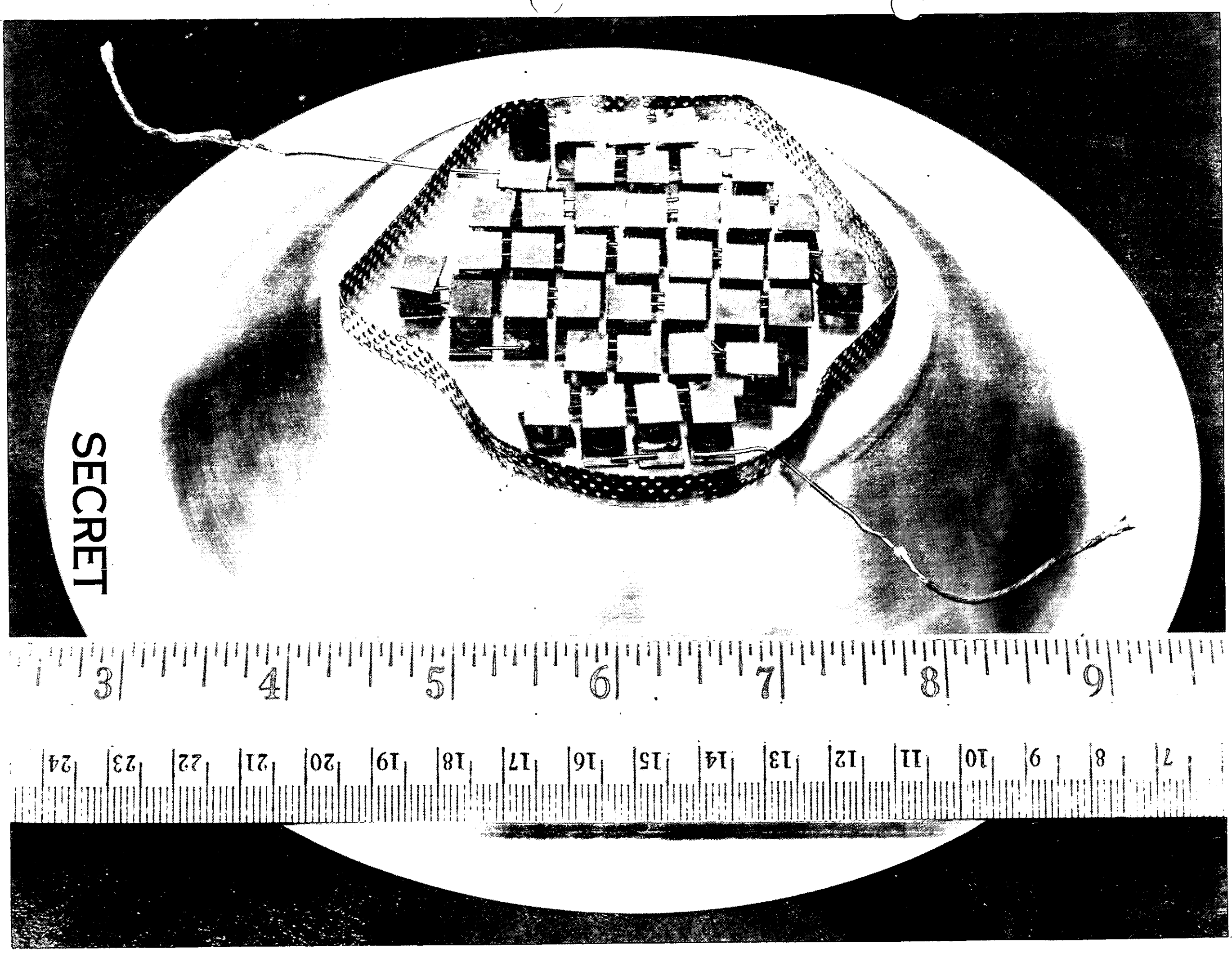

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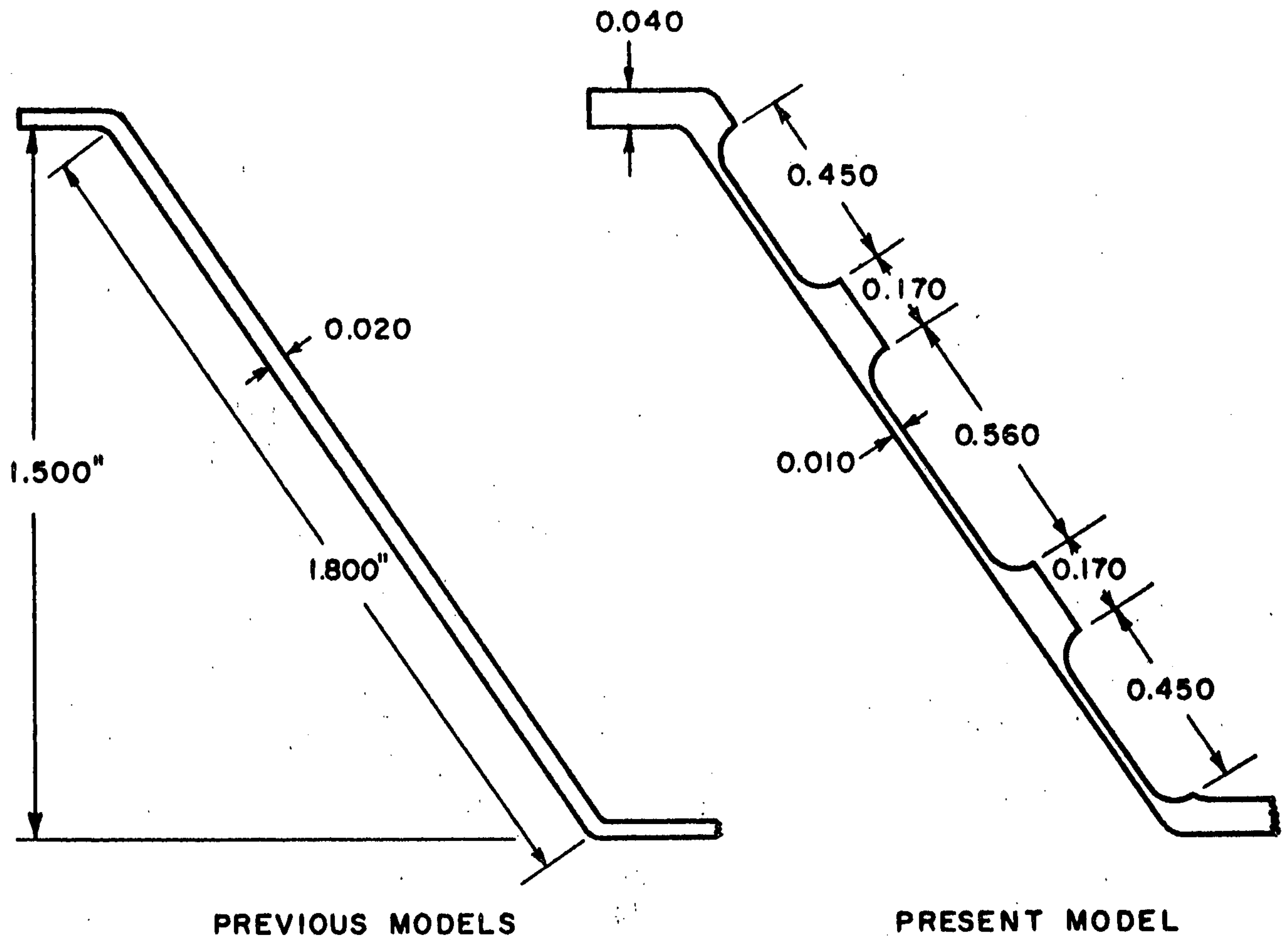
PLACEMENT OF THERMOELECTRIC GENERATOR AND PROTECTIVE "FENCE" IN RELATION TO UPPER PAN that use of a continuous strip of perforated nickel would result in more reliable mechanical design combined with greatly reduced thermal conductance. In addition, the one-piece fence greatly simplified the assembly procedure.

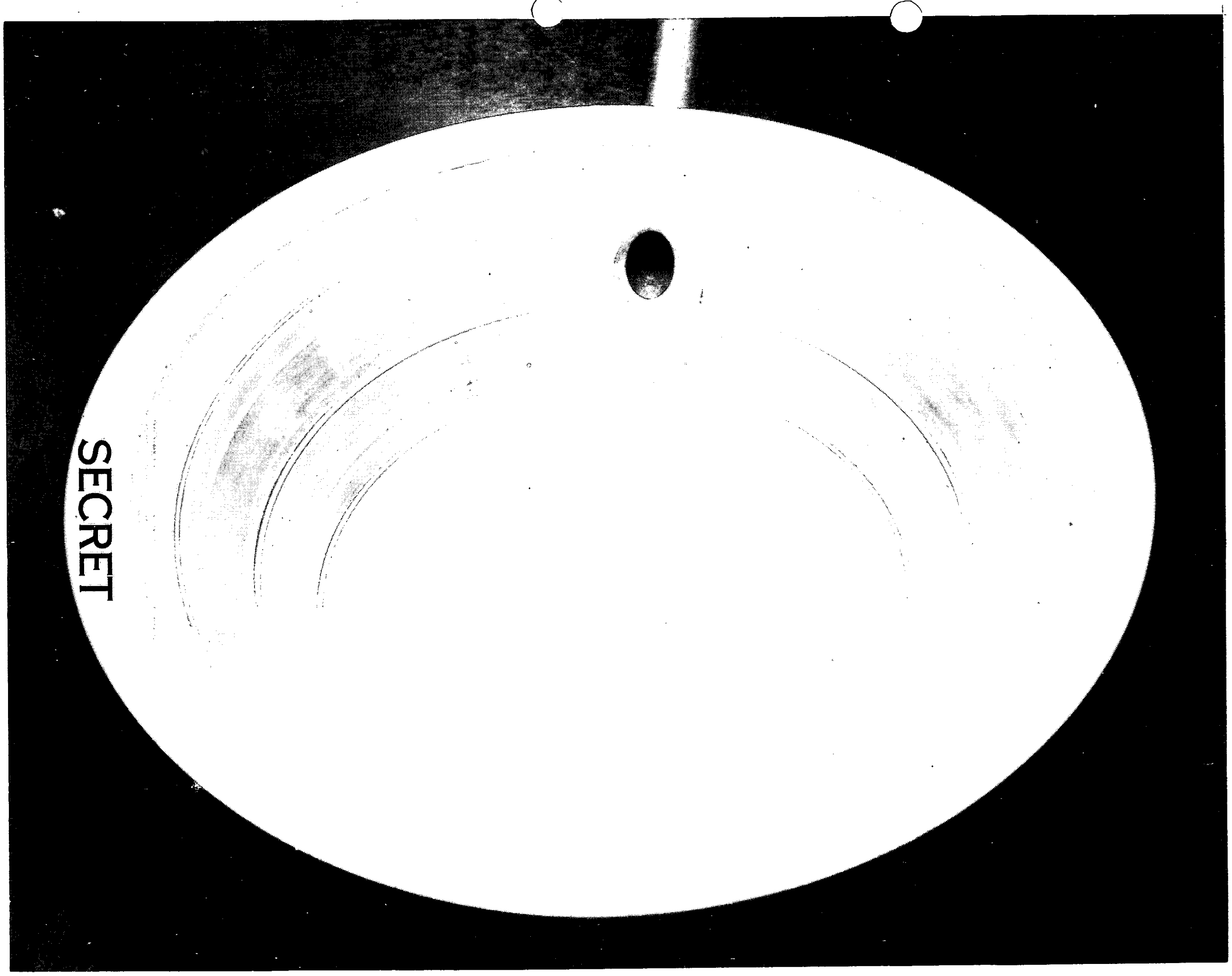
To make full use of the heat reaching the hot side of the container it is essential that the temperature of the lower pan be as uniform as is practical. Previous designs utilized brass of 0.025-inch thickness for both the upper and lower pans. It was found however that the thin metal produced severe inhomgeneities in the temperature of the lower pan. In order to diminish the inhomogeneities, the present device was designed with a lower pan 0.040 inch thick. To minimize the flow of heat up the side of the lower pan (a thermal short-circuit) sections of the side were reduced to 0.010 inch thick. The side-walls of this model and of the previous design are shown in Figure 5. The thermal conductance of the side of the lower pan is diminished to about two-thirds that of the first model. The lower pan, with its handle attached, is shown in Figure 6. Here may be seen the stiffening bands left in the side of the pan. By use of this technique, the mechanical strength of the completed device is not impaired while the design is markedly improved.

To realize the smallest difference in temperature between the cold junction of the generator and the cooling water, the circular bottom of the upper pan was reduced in thickness to 0.020 inch. This



COMPARISON OF CROSS-SECTIONS OF SIDE WALLS OF LOWER PANS

FIGURE 5



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INTERIOR OF LOWER PAN, SHOWING THINNED BANDS was accomplished by precise acid-etching under controlled conditions. All portions of the upper pan except its bottom were of 0.025-inch brass. In such a way mechanical strength of the external and internal portions of the container were increased, along with the potential thermal efficiency.

V. PREPARATION AND EVALUATION OF MATERIALS

In the development of the previous thermoelectric generator, it became apparent that there were serious discrepancies between the performance of the actual device and its predicted performance. Some of these differences could be traced to the non-ideal design, while others were attributed to the properties of the materials used in the generator itself. It was therefore deemed advisable to enforce strict measures of control to assure a performance in the present device which would not differ widely from prediction. These safeguards took the form of careful synthesis of the materials employed, as well as introduction of measurements of the properties of the materials, to avoid inclusion of inferior semiconductors in the device.

A. Preparation of Materials The procedure for preparation of zinc antimonide was generally that employed for the previous model. Zone-refined antimony (at least 99.999 per cent pure), freshly-recast zinc (99.99 per cent pure), and a doping alloy prepared from bismuth, tin, and silver (all at least 99.98 per cent pure) were the starting materials. The melt consisted of zinc and antimony in a molar ratio of 1.01:1.00, to which was added a sufficient quantity of the doping alloy to yield additions (by weight) of 1.00 per cent bismuth, 1.00 per cent tin, and 0.05 per cent silver. Melting took place in a sealed and evacuated Vycor tube at a temperature of approximately 650° C for one hour, with frequent agitation. The molten mixture was cooled in the furnace to

480° C and allowed to anneal for 24 hours, after which it was removed from the furnace. After measurement of the properties of the ingot, it was sawed into pieces for re-casting in a cylinder with the desired five-millimeter diameter, and re-annealed.

Lead telluride was also prepared in Vycor vessels. To prevent sticking of the compound to the Vycor, the container was coated with a thin layer of finely-divided graphite, evacuated, filled with hydrogen, and heated to bright red heat. This treatment removed any oxygen adsorbed on the surface of the silicaceous material, thereby preventing the oxdiation which could ruin an entire batch of lead telluride. The lead employed was 99.99^{+} per cent pure. Tellurium, obtained as 99.95 per cent pure, was distilled in an atmosphere of flowing hydrogen, to assure freedom from tellurium dioxide. Additions of 0.05 weight per cent of bismuth (99.99 per cent pure) were included in the stoichiometric mixture of lead and tellurium.

Because lead and tellurium react exothermally to form a compound whose melting point is higher than that of its constituents, great care had to be taken to prevent cracking of the vessels employed for the reaction. A Vycor vessel containing the solid ingredients in an atmosphere of hydrogen at a pressure of 100 mm Hg, was placed in a furnace at a temperature of approximately 1025° C. Any lead telluride produced was in the molten state, since the melting point of the compound is approximately 930°C. The furnace temperature was lowered to 700° C and the compound annealed at this temperature for 24 hours.

After its properties had been measured, the ingot was sawed into pieces for re-casting.

In order to compare the performance of bonded pieces of lead telluride produced in the laboratory with bonded materials of commercial quality, a number of bonded pieces were purchased from the Minnesota Mining and Manufacturing Company. The chief difference between the "3M" product and the local lead telluride lay in the method of bonding to the contact piece at the hot side. The method used in the laboratory was the same as that used for bonding zinc antimonide: essentially it was a soldering operation using resistance-heating to cause the solder to flow. (This method has been described in detail in the course of the development program for the previous thermoelectric generator.) The "3M" specimens were cast directly on the contact piece. In order to avert the destructive effects of the difference in thermal expansion between the contact piece and the lead telluride, "3M" uses a special alloy of 96% iron and 4% molybdenum. On the cold side, the "3M" pieces were soldered in a manner similar to that employed locally.

It was found that both methods of preparing bonded lead telluride were nearly equivalent. Because of the convenience of assembling the "3M" bonded specimens into a complete generator, they were selected for use in the finished product.

B. Measurements Initially, it had been planned to make detailed measurements of the Seebeck coefficient and electrical resistivity of all materials included in the finished thermoelectric generator.

However, experience has shown that within relatively narrow limits, a given value of one property corresponds to a particular value of the other. Because the measurement is relatively simple, it was therefore decided to measure only the resistivity of the semiconductor to be employed. A four-probe fixture was constructed which permits the measurement of electrical resistivity of a bar at intervals of 0.050 to 0.010 inch. By measuring the entire length of a 6 to 10 inch bar at these close intervals, it is possible to obtain a profile of the resistivity of the specimen as a function of its length. A typical example of such a profile is shown in Figure 7. It can be seen from the graph that certain portions of the bar exhibited remarkably uniform electrical resistivity. Those portions containing inhomogenities in the electrical resistivity were not used in the construction of the thermoelectric generator.

Of equal practical importance to the performance of the completed generator is the absence of contact resistance. Another fixture for determination of the contact resistance at each end was constructed. The method is essentially one of extrapolation of the resistance-vs.-length curve to the ends of the bonded specimen. Any disparity between the intersections of the curve with two ordinates is taken to represent the contact resistance. A typical set of data is shown in Figure 8. It can be seen that the total resistance introduced at the contacts is of the order of 5% of the resistance of the semiconductor itself.

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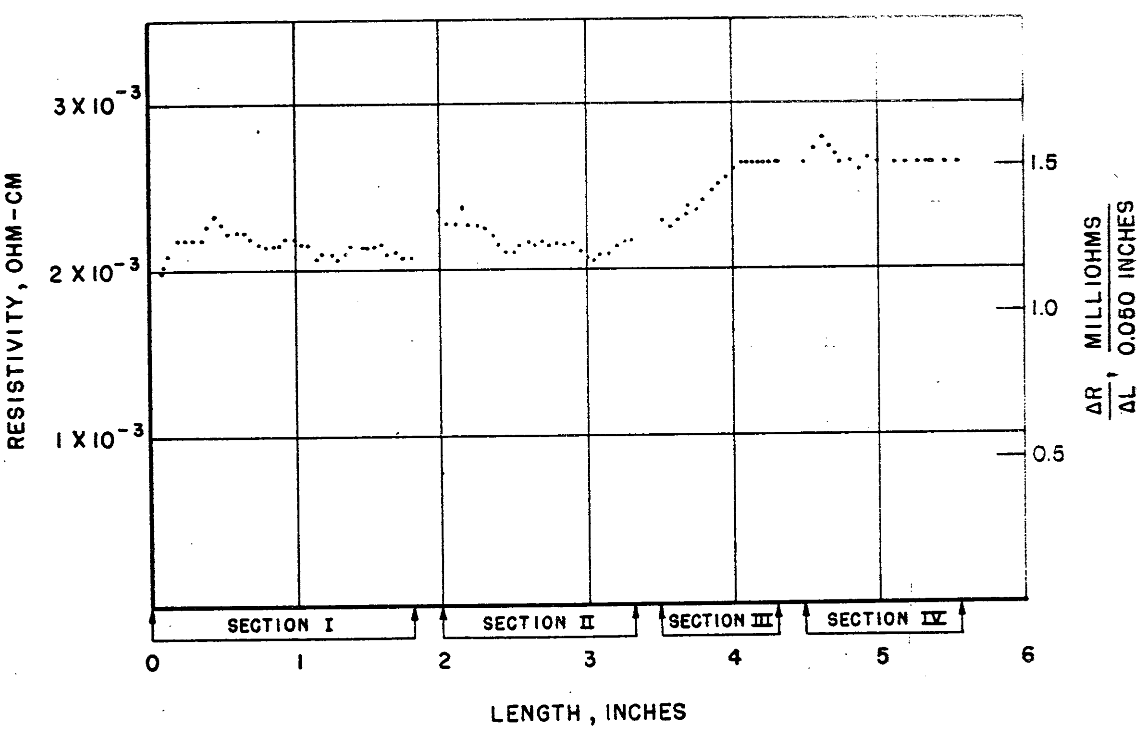

RESISTIVITY OF CAST BAR OF ZINC ANTIMONIDE AS FUNCTION OF LENGTH

FIGURE 7

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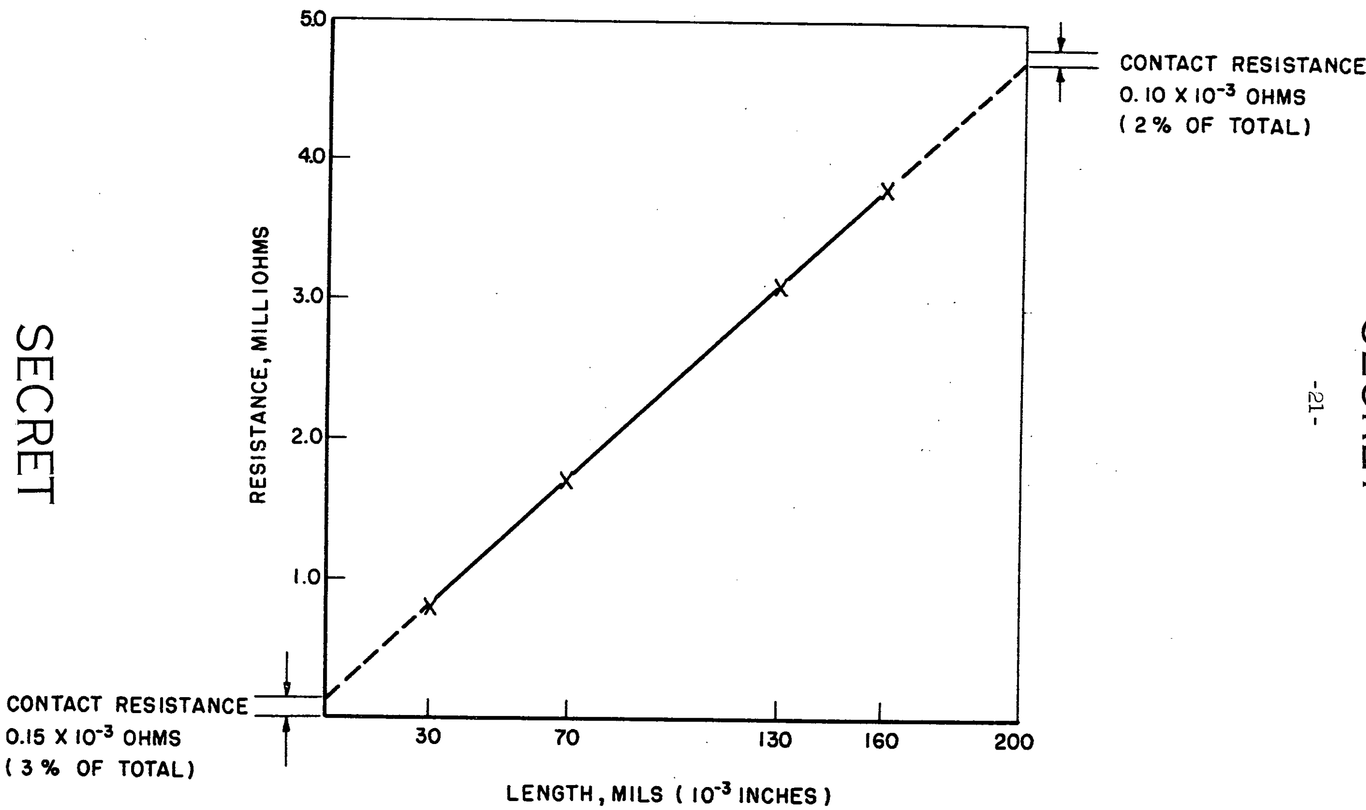

TYPICAL MEASUREMENT OF CONTACT RESISTANCE OF BONDED ZINC ANTIMONIDE

FIGURE 8

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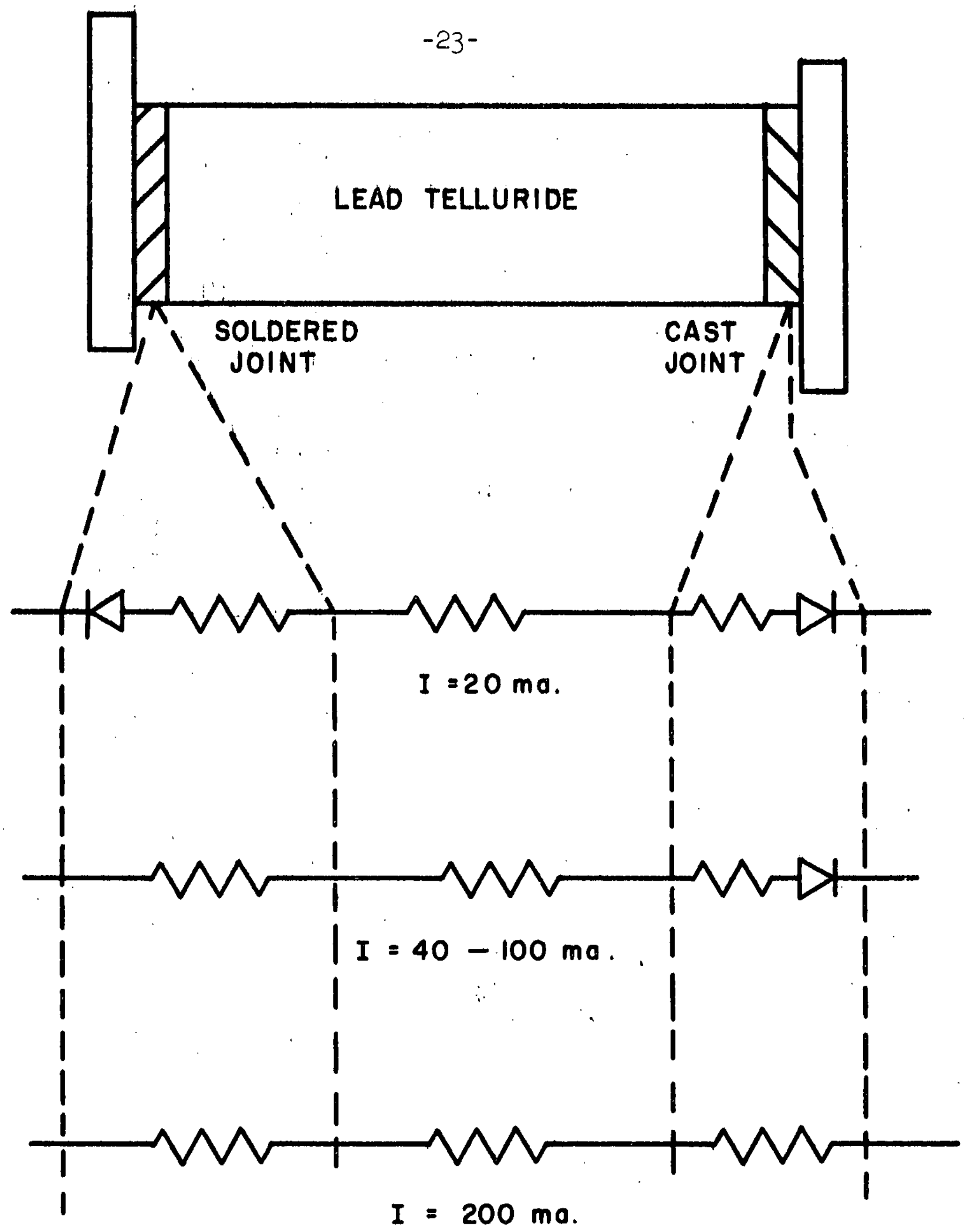
In the course of contact-resistance measurements, it was found that the lead telluride specimens manufactured by the Minnesota Mining and Manufacturing Company exhibited distinct rectifying properties at low currents. As shown in Figure 9, the phenomenon was present both in the soldered and cast bonds at very low currents, disappeared from the soldered joint at intermediate currents and was completely absent when current in excess of 200 milliamperes was flowing through the specimen. Although of academic interest, the observation is of little practical importance, since the completed device is intended for use with currents far in excess of 200 milliamperes.

When the generator had been assembled, but prior to its installation in the container, it was found desirable to make a spot-check of the Seebeck coefficients of individual couples. This was accomplished by maintaining one side of the investigated couple at room temperature, while cooling the other side of the couple by application of ice. The Seebeck coefficients observed for couples lay in the range 385 to 400 microvolts per degree Celsius. Considering the crudeness of the measurement, this is quite close to the theoretical value of 425 microvolts per °C. The conclusion drawn from such measurements was that the spot-welding of the copper connectors had not affected the semiconductors adversely.



CONVERSION TO OHMIC CONTACTS WITH INCREASING CURRENT

FIGURE 9

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VI. PERFORMANCE OF COMPLETED GENERATOR

Three properties of the completed thermoelectric generator are of interest: the performance under load, the power delivered as a function of temperature, and the efficiency of conversion of thermal energy to electrical energy. In order to determine these properties, the assembled generator was placed upon a pan of Arochlor 1248 (manufactured by Monsanto Chemical Co.) and heated. The Arochlor served as a heat-transfer medium at temperatures up to approximately 330° C. Above this range, a gas burner was used directly as the source of heat. The temperature of the lower pan was determined by means of a thermocouple whose bead was cemented directly to it. The temperature of the upper pan was found by measurement of the water temperature with a thermometer. The technique for measurement of current and voltage was the same as that employed in testing the previous model.

Figure 10 shows the output voltage of the present generator as a function of the current drawn*. When compared with the previous model, it can be seen that the expected doubling of the open-circuit voltage by

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* Performance data reported in this section were taken prior to the catastrophic overheating of the generator as originally built. The overheating was the result of placing the bottom of the generator in contact with a large burner whose maximum temperatures was later found to be in excess of 900° C. Upon rebuilding the generator, it was found that the output and efficiency were reduced by approximately 15%. These facts may explain any discrepancy between the observations reported here and thosewhich may be made on the device as delivered to the sponsor.

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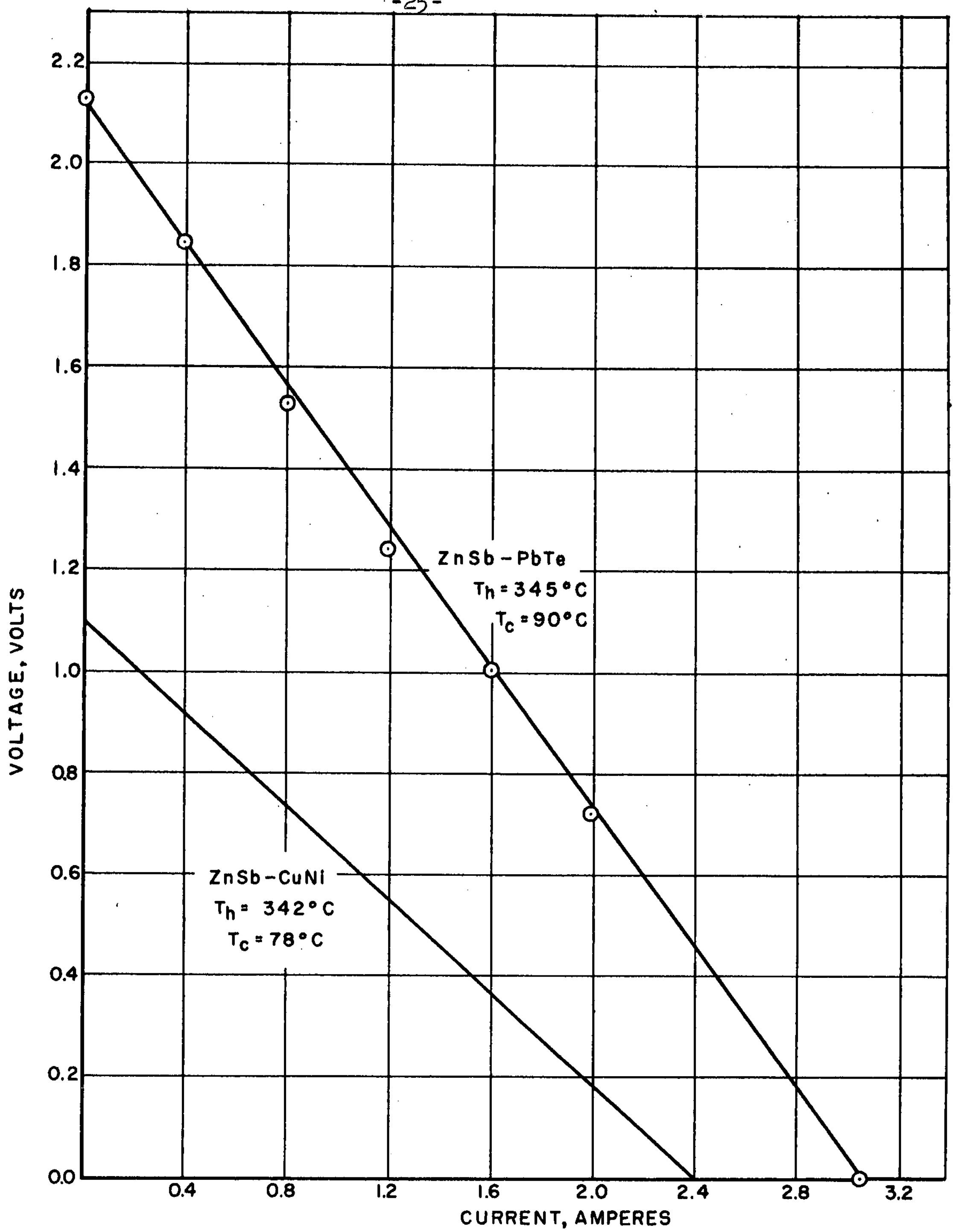
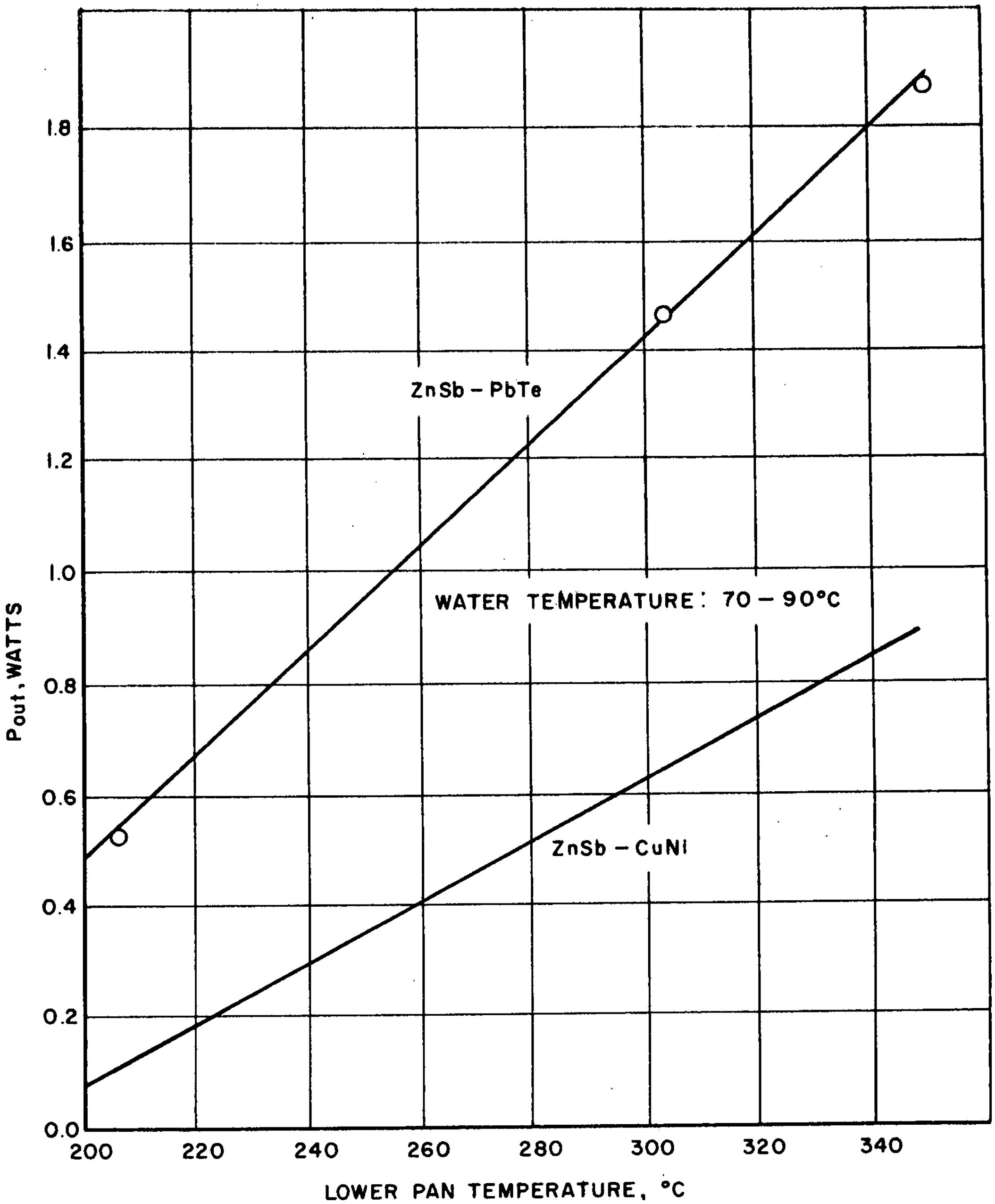


OUTPUT OF TWENTY-COUPLE THERMOELECTRIC GENERATORS AT NORMAL OPERATING TEMPERATURES.

FIGURE 10



DEPENDENCE OF OUTPUT TWENTY-COUPLE THERMOELECTRIC GENERATORS ON HOT-SIDE TEMPERATURE

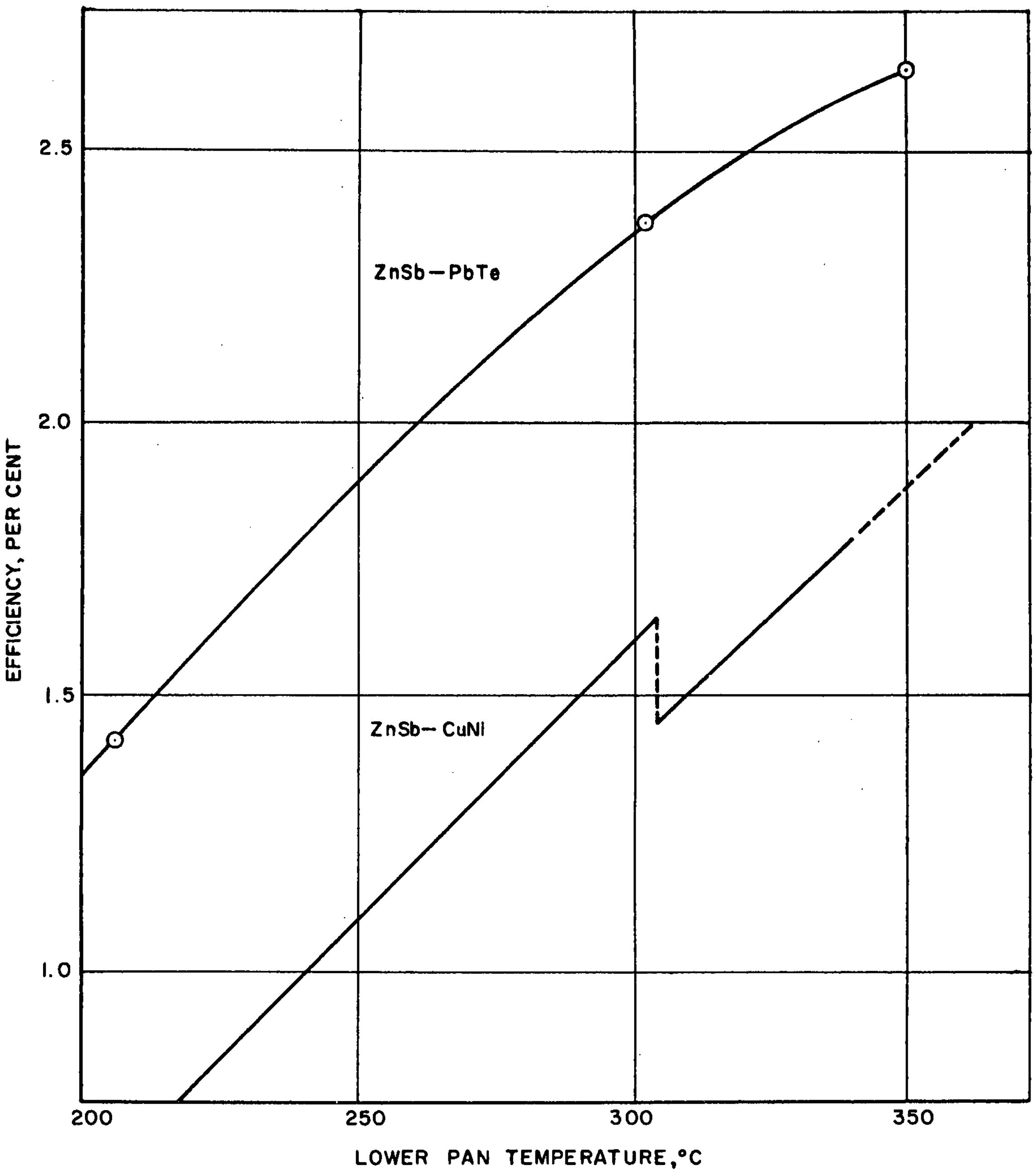
FIGURE 11

replacement of the Advance with lead telluride actually did take place. It is interesting to note that, although the designed short-circuit current was 3.0 amperes, the observed value was slightly higher than that figure.

The dependence of the power available from the thermoelectric generator as a function of the temperature of the lower pan is shown in Figure 11. It can be seen that the output of the present model at any given temperature is more than twice that of the previous model. This condition is the result of two chief factors. First of all the substitution of lead telluride for Advance greatly enhances the output voltage. Second, the use of copper leads (rather than nickel) in the generator greatly decreases the resistive losses.

The efficiency of the two devices is compared in Figure 12. The efficiency as shown here is calculated from the thermal conductance of the generator itself, and does not include the losses in the container. Measurements of the heat flowing through the container show that the losses in the present model were only between 50 and 60 per cent of those in the previous model. This means that the utilization of the heat striking the lower pan is between two and three times as effective in the present thermoelectric generator.

One may conclude, from the performance of the present device, that the improvements in performance sought in the present development program have been achieved. Some additional improvements might result from refinements in design. These will be discussed in the next section.



EFFECT OF HOT-JUNCTION TEMPERATURE ON EFFICIENCY OF TWENTY—COUPLE GENERATOR

FIGURE 12

VII. FUTURE DEVELOPMENTS

As has been pointed out in previous reports, the twenty-couple thermoelectric generators produced to date were intended as prototypes for the production of larger generators containing 240 couples. On the basis of the performance indicated in Figures 10 and 11, one may predict that such a 240-couple generator could be produced with an open-circuit voltage of 25 volts and a short-circuit current of approximately three amperes, or an output power of approximately twenty watts at the present operating temperatures. Should it be deemed desirable to pursue such a development program, several modifications could lead to enhanced reliability, lower cost and lighter weight of the completed device. The improvements may be categorized as those of material preparation and those of design and construction techniques.

A. Improvements in Materials The present selection of zinc antimonide and lead telluride as the active portions of the thermoelectric generator appears satisfactory. In order to improve the reliability and resistance to overheating of the device, it may be desirable to encapsulate the individual pieces of semiconductor in a protective ceramic cylinder. Such encapsulated specimens have been prepared in this Laboratory with the electrical contact being made directly between the semiconductor and a metal plate at each end of the hollow ceramic cylinder. One advantage of encapsulation lies in the simplicity of fabrication of the individual arms of a couple. Moreover, in the encapsulated form, a semiconductor is protected from the deleterious effects of oxygen. In this manner, simplicity and reliability would both be increased.

One of the greatest difficulties in the preparation of the bonded semiconductor pieces is in the sawing of the semiconductor itself. Becuase of the preferred cleavage of the relatively large crystals found in a bar of cast zinc antimonidce or lead-telluride, chipping of the piece occurs frequently in the sawing. Were it possible to reduce the size of the crystallites, the tendency to cleave would be greatly diminished. One method for achieving small crystal size may be the application of powder-metallurgical techniques to the production of bars of semiconductor. If such destructive cleavage could be eliminated, the cost of production of pieces ready for bonding would be drastically reduced. An additional advantage would result from the possibility of re-using scrap material for production of useable couples.

A third area in which improvements in the materials are possible may lie in casting both <u>n</u>-type and <u>p</u>-type lead telluride on the same contact piece. In addition to reducing the number of soldered contacts in the generator, this modification could result in a smaller volume required for the generator itself. The use of <u>p</u>-type lead telluride as a direct substitute for zinc antimonide is feasible because of the great similarity of the properties of the two materials in this temperature range.

<u>B. Improvements in Design and Manufacturing Techniques</u>

The chief advantage in the [redacted] of the container of the 25X1

thermoelectric generator comes from the heat leaking up the sides from the lower pan to the upper pan. A change in design which would improve the efficiency and also eliminate the necessity for a supporting fence is shown in Figure 13. Not only is virtually all the heat striking the [redacted] transmitted through the thermoelectric generator to the 25X1
cooling water, but several other advantages may be found in this design. For example, the construction shown in the sketch would make it possible to use welding, rather than soldering as the means of enclosing the generator. Stamped upper and lower "bottoms" could be so devised so that they would be capable of being welded together, and then the resulting package could be affixed to the dome of the [redacted] by a rolling 25X1
technique, as is done in some commercially-available [redacted] Alter- 25X1
natively, it may be advantageous to extend the double bottom a few inches along the side-walls, thereby reducing thermal losses to an absolute minimum. A final advantage accruing from the [redacted] 25X1
design is that it permits a larger fraction of the area of the bottom to be used for inclosing the generator. It may be estimated that a 240-couple generator could be inclosed in a [redacted] whose bottom is 25X1
approximately eight inches in diameter.

Whatever further developments may be projected in this program, it seems advisable to include in the next step the evolution of some techniques suitable for manufacturing large numbers of devices. The present program has demonstrated the feasibility of the thermoelectric

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system and the general design of the thermoelectric generator. Future development programs would have as their objective the demonstration of the feasibility of manufacture of several units on a pilot-operation scale.

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